

ISSN 1848-0071
669.334+661.666=111
Received: 2014-07-11
Accepted: 2014-08-14
Original scientific paper

PRECONCENTRATION OF COPPER FROM SYNTHETIC AQUEOUS SOLUTIONS USING MULTIWALLED CARBON NANOTUBES

JANA SEMANČIKOVÁ, DAGMAR REMETEIOVÁ

Technical University of Košice, Faculty of Metallurgy, Košice, Slovakia

e-mail: jana.semancikova@tuke.sk

The determination of heavy metal contents in various components of the environment is very important in the context of environmental protection. In laboratory practice often happens that the determination of trace and ultra-trace contents of heavy metals in natural aqueous samples by available method is not sufficient with respect of required accuracy. In such cases it is necessary to include appropriate treatment of the samples prior to their analysis. For the purpose of preconcentration of the trace metal content the solid phase extraction (SPE) is often used. Carbon nanotubes (CNTs) are considered to be suitable sorbent material enabling increase the separation and preconcentration efficiency of SPE over other conventional silica-based sorbents. This work includes the evaluation of experimental conditions (pH of sample solution, content of the analyte, method used for CNTs oxidation and amount of solid sorbent) used in SPE-CNT preconcentration of copper from synthetic aqueous solutions.

Key words: copper, multiwalled carbon nanotubes, solid phase extraction.

Prekoncentriranje bakra iz pripravljenih vodenih otopina uporabom višeslojnih ugljičnih nanocjevčica. Određivanje sadržaja teških metala u okolišu vrlo je važno u kontekstu zaštite okoliša. U laboratorijskoj praksi se često događa da raspoložive metode s obzirom na zahtjevanu točnost nisu dovoljne za određivanje sadržaja teških metala u tragovima i ultra-tragovima u prirodnim vodenim uzorcima. U takvim slučajevima potrebno je provesti odgovarajući tretman uzoraka prije analize. Za potrebe prekoncentriranja metala u tragovima često se koristi ekstrakcija iz čvrste faze (SPE). Ugljikove nanocjevčice (CNT) smatraju se prikladnim materijalom – sorbentom koji omogućava povećanu učinkovitost SPE u pogledu separacije i prekoncentriranja u odnosu na druge konvencionalne sorbente na bazi silikona. Ovaj rad sadrži procjenu eksperimentalnih uvjeta (pH otopine uzorka, sadržaj analita, metode koja se koristi za oksidaciju te količine čvrstog sorbensa CNT) pri kojima je provedeno prekoncentriranje bakra iz pripravljenih vodenih otopina uporabom ekstrakcije iz čvrste faze uz pomoć ugljikovih nanocjevčica (SPE-CNT).

Ključne riječi: bakar, višeslojne ugljikove nanocjevčice, ekstrakcija čvrste faze.

INTRODUCTION

The determination of heavy metal contents in the environmental samples plays an important role in the context of environmental protection. Often the direct determination of the metal content in complex matrices of samples is limited due to their low (trace to ultra-trace) concentrations and matrix interferences. Therefore it is necessary to include preconcentration and separation of metals, in

the trace analysis, leading to increase the sensitivity and selectivity of their determination. In the past years, several treatments for enrichment and preconcentration of analytes followed with subsequent determination by one of an atomic spectrometry methods have been proposed and applied.

Among preconcentration methods, the methods based on the extraction with

solid sorbent or Solid Phase Extraction (SPE) methods are proved to be the most suitable. SPE offers a number of important benefits in comparison with classical liquid-liquid extraction, such as simple and fast extractor system, utilization of reduced solvent amount and their exposure, low disposal costs, ability of treating large sample volumes free from contamination, rapid phase separation, and the possibility of combination with different analytical techniques [1, 2, 3]. In both kinds of SPE (batch and column techniques) analytes are sorbed on different water-insoluble materials (solid sorbents) and eluted mostly with acid reagents [3]. A typical solid phase extraction cartridge consists of a short column

(generally an open syringe barrel) containing a sorbent packed between porous materials or plastic frits (Figure 1) [4]. The choice of proper sorbent should be based on the type of analyte, sample matrix and technique for final determination [5]. Variety of materials are used as solid sorbents in SPE, such as cellulose, bonded or modified silica, activated carbon, polyurethane, alumina, exchange resins, zeolites etc. [6]. Among carbon-based sorbents, activated carbon was one of the first materials applied in SPE, but more recently, much attention has been paid to carbon nanostructure materials of different chemical composition such as carbon nanotubes (CNTs) [5].

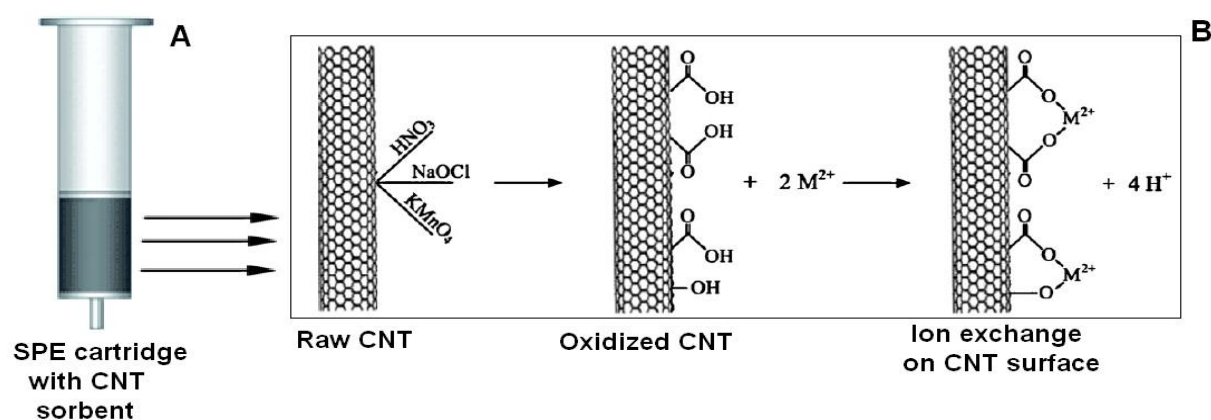


Figure 1. (A) SPE cartridge with CNT sorbent and (B) schematic diagram of divalent metal ions sorption onto CNT surface [5, 9]

Slika 1. (A) Modul za SPE s CNT kao sorbentom (B) shematski dijagram sorpcije dvovalentnih metalnih iona na površini CNT

Carbon nanotubes are relatively a new material, which have in recent years obtained wide attention in the field of analytical chemistry. Strong interactions of hexagonally grouped carbons in graphene sheets of CNTs, with other molecules and large specific surface area make this material a promising solid sorbent for preconcentration procedures [7]. In contrast to the activated carbon, CNTs have a well-defined

structure at atomic scale, so reproducible results of metal preconcentration can be achieved [8]. Carbon nanotubes can be divided into two categories: singlewalled CNTs (SWCNTs) which look like hexagonal sheets of graphite rolled into cylindrical tubes and multiwalled CNTs (MWCNTs) consisting of several concentric SWCNTs [9, 10].

EXPERIMENTAL

Metal ions in an aqueous medium are not capable of adsorption on the surface of non-modified carbon nanotubes, and therefore it is necessary to modify them. The simplest form of modification of the carbon nanotube surface is oxidation process. This process forms free oxygen functional groups on the surface of CNTs (for example -OH, -C=O, -COOH), and consequently causes their increased solubility in aqueous media [8]. These functional groups containing oxygen radicals are capable of binding metal

ions at a suitable pH. The oxidation of nanotubes can be carried out with acid reflux with HNO₃, H₂SO₄, HCl, or with oxidizing agents such as KMnO₄ and H₂O₂ [6]. The literary overview of carbon nanotubes oxidation methods, before utilizing them as a solid sorbent, is given in Table 1.

In our experiments, we have chosen to oxidize carbon nanotubes with 8 mol dm⁻³ HNO₃ for 12 hours at room temperature, which was according to the studied literature proposed by A. Stafiej et. al. [1].

Table 1. Oxidized carbon nanotubes applied in preconcentration of metal ions

Tablica 1. Oksidirane ugljične nanocjevčice korištene za prekoncentriranje metalnih iona

Oxidation reagent	V _{reagent} [cm ³]	m _{CNTs} [g]	Time [h]	Temperature [°C]	Note	Reference
conc. HNO ₃	-	-	1	25	reflux	[7]
conc. HNO ₃	30	3	12	25	-	[11]
conc. HNO ₃	-	-	1	25	reflux	[12]
conc. HNO ₃	50	5	5	80	reflux	[13]
conc. HNO ₃	25	1	6	100	-	[14]
HNO ₃	-	-	5	80	reflux	[8]
8 mol dm ⁻³ HNO ₃	50	2	12	25	-	[1]
3 mol dm ⁻³ HNO ₃	-	-	-	-	low-power	[5]
30 % H ₂ O ₂	-	-	-	-	sonochemical treatment	

The process of oxidation also increases the possibility of further modification and functionalization of the graphitic surface [5]. Modified CNTs can be prepared through loading with chemical modifier or through chemical functionalization. In the first case, CNTs are loaded with chelating agent that is not chemically bonded to the CNT surface. In

the second case, chemical groups, which can form complexes with metal ions, are chemically bonded to the CNT surface [8]. In Table 2 are shown examples of chemical modification of oxidized multiwalled carbon nanotubes with EDA (ethylenediamine) [19] or with PAN (1-(2-pyridylazo)-2-naphtol) loading [20].

Table 2. Modified and non-modified carbon nanotubes applied in preconcentration and determination of metal ions**Tablica 2.** Modificirane i nemodificirane ugljične nanocjevčice korištene za prekoncentriranje i određivanje metalnih iona

Element	Sorbent type	Eluent	Elution flow rate [cm ³ min ⁻¹]	Detection technique	Reference
Au(II)	MWCNT	3 % thiourea in 1 mol dm ⁻³ HCl	0.5	F-AAS	[7]
Au (II), Mn(II)	MWCNT- NBHAE	0.1 mol dm ⁻³ Na ₂ S ₂ O ₃	1	F-AAS	[11]
Rare earth elements	MWCNT	1 mol dm ⁻³ HNO ₃	-	ICP-OES	[12]
Cu(II)	MWCNT 10-15 nm	2 mol dm ⁻³ HNO ₃	-	F-AAS	[15]
Cu(II), Cd(II)	MWCNT- APDC	HNO ₃ + Acetone	5	F-AAS	[16]
Cu(II), Pb(II)		3 mol dm ⁻³ HNO ₃	3	F-AAS	[17]
Cu(II)	MWCNT	2 mol dm ⁻³ HNO ₃	2	F-AAS	[18]
Mn(II)	MWCNT- PAN	0.1 mol dm ⁻³ HNO ₃	1	F-AAS	[19]
Cr(III), Pb(II)	MWCNT- EDA	1 mol dm ⁻³ HCl	-	ICP-OES	[20]

APDC Ammonium pyrrolidine dithiocarbamate, EDA Ethylenediamine, NBHAE N,N'-bis(2-hydroxybenzylidene)-2,2'-(aminophenylthio)ethane, PAN 1-(2-pyridylazo)-2-naphthol, F-AAS Atomic absorption spectrometry with flame atomization, ICP-OES Inductively coupled plasma optical emission spectroscopy

Experimental conditions

Synthetic aqueous solutions of copper were prepared from certified water stock solutions with concentration 1.000 ± 0.002 g dm⁻³ of copper. Copper determinations in sample solutions were carried out on Perkin Elmer 3030 atomic absorption spectrometer with flame atomization. Multiwalled carbon

nanotubes MWCNTs (> 95 % purity, 10 – 20 nm outer diameter, 10 – 30 μm length) used in experiments were purchased from Chengdu Organic Chemicals Co. Ltd.. For adjusting the required pH values, aliquots of concentrated ammonium hydroxide NH₄OH were added to the sample solutions.

RESULTS AND DISCUSSION

The aim of this work was to optimize selected experimental conditions of novel and simple method of preconcentration for selected metal ion Cu(II) using carbon

nanotubes as a solid sorbent, before its determination by atomic absorption spectrometry with flame atomization.

pH of sample solution

As was mentioned above, nitric acid oxidation of carbon nanotubes leads to functionalization of the surface, and hence to the creation of functional groups containing oxygen radical. The surface charge of nanotube depends on the pH of surrounding electrolyte [1]. The sorption of metal ions on surface of the oxidized nanotubes increases in general with increasing pH. The surface of carbon nanotubes at higher pH is more deprotonated ($-\text{COOH} \rightarrow -\text{COO}^-$), which causes electrostatic interactions between metal ion Me(II) and oxygen functional group [8]. Sorption of the analyte onto surface of CNT varies with the metal ion to be sorbed. It was shown [1, 8], that within the range of pH 7 – 9, affinity of metal ion to

CNTs surface is decreasing in this order: Cu(II) , Pb(II) , Zn(II) , Co(II) , Ni(II) , Cd(II) .

To determine the optimal value of sample solution pH for the CNT preconcentration, we have chosen synthetic aqueous solutions of two metal ions Cu(II) (highest affinity to CNTs) and Cd(II) (lowest affinity to CNTs) to be adsorbed onto 200 mg of the solid CNT sorbent. The dependence of 200 μg Cu recovery on pH of the sample solution in pH range of 7.5 – 10.0 is shown in Figure 2 (A) and the dependence of recovery of 2000 μg Cd on the pH of the sample solution in the same pH range is shown in Figure 2 (B). Highest recovery was achieved by preconcentration metal ion at pH of 9.5 in both cases.

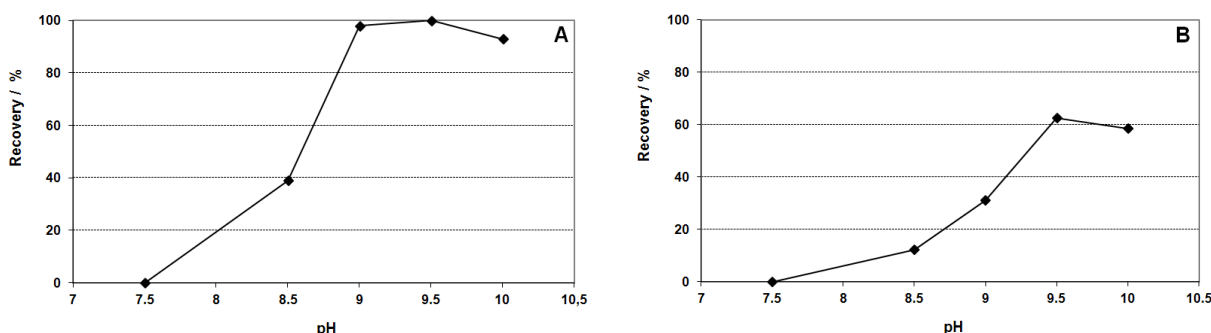


Figure 2. Dependence of (A) 200 μg Cu recovery and pH of sample solution, (B) 2000 μg Cd recovery and pH of sample solution

Slika 2. Ovisnost (A) 200 μg povratnog Cu o pH otopine uzorka, (B) 2000 μg povratnog Cd o pH otopine uzorka

Amount of analyte

The effect of analyte amount to be adsorbed onto 200 mg of CNTs to Cu recovery is graphically shown in Figure 3. In this case, recoveries of Cu after preconcentration on CNTs solid sorbent in column and also bath experiments were studied. Highest (100 %) recovery of Cu was observed in the column and bath

arrangement with the Cu content of 200 μg . With increasing Cu content, recoveries decreased due to the depletion of sorption capacity of given solid sorbent quantity (200 mg CNTs). We could avoid this effect by selecting different oxidation process of CNTs to create more free functional groups on the surface, such as the use of ultrasound

assisted oxidation as indicated author Pryzinska, K. [5] in her work. The recovery in bath arrangement SPE was almost 100 % even at 400 ppm Cu content, compared to the column method in which it was only 94.8 %. This phenomenon could be due to the

fact that in column arrangements, the sorption rate at which sample flows through column affects the recovery, while in bath arrangements, sample is constantly in contact with sorbent over whole experimental time, in our case it was three hours.

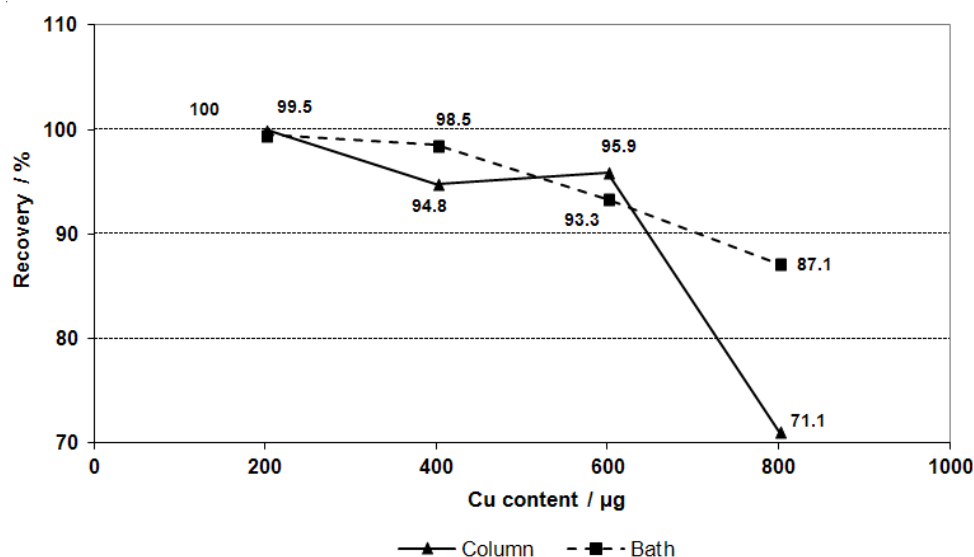


Figure 3. Dependence of Cu recovery on Cu content in column and bath arrangement CNT-SPE
Slika 3. Ovisnost povratnog Cu o sadržaju Cu u izvedbama CNT-SPE u obliku kolone i kupke)

Concentration of eluent

The metal ions adsorbed on oxidized CNTs can be quantitatively eluted with acidic eluting agent. Low pH of the eluent results in quantitative elution due to the competition between protons and metal ions [8]. Most commonly used elution agents and their concentrations are shown in Table 2.

The effect of the elution reagent concentration onto the eluent efficiency of the analyte was monitored by preconcentration and elution of 200 μg Cu from

synthetic aqueous solutions. The analyte intercepted onto 200 mg CNTs solid sorbent was eluted by 5 cm^3 of nitric acid with concentration in the range of 1 – 5 mol dm^{-3} HNO_3 . The highest elution efficiency we obtained by eluting was with 5 cm^3 of 2 mol dm^{-3} HNO_3 , but this was only cca 90 %. To increase the elution efficiency it would be appropriate to test another type of eluent or increase the elution volume.

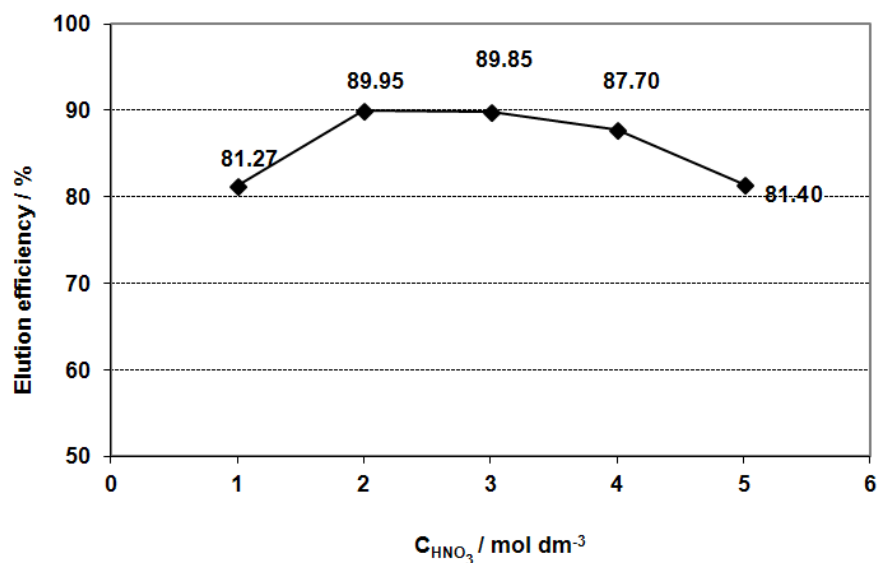


Figure 4. Dependence of elution efficiency of Cu on concentration of eluent (HNO_3)

Slika 4. Ovisnost efikasnosti eluiranja Cu o koncentraciji eluenta (HNO_3)

CONCLUSION

Since their discovery in 1991, carbon nanotubes have gained great attention of the scientific community, due to their wide applicability in analytical chemistry. Their significant sorption and desorption capacity predestined them for use as a solid sorbent material in extraction and preconcentration of metal species from various liquid media [8]. The impact of selected experimental conditions of the SPE-CNT extraction on the recovery of copper from synthetic aquatic solutions was studied in this work. Based on the experimental results, the following conclusion can be stated:

1. The experiments showed that with increasing pH, the analyte sorption efficiency of solid sorbent increased.
2. The optimum pH for sorption of Cu(II) was determined at $\text{pH} = 9.5$.

3. Highest elution efficiency of captured analytes was obtained with 5 cm^3 of $2 \text{ mol dm}^{-3} \text{ HNO}_3$, but this efficiency was only cca 90 %.
4. In the terms of analyte sorption efficiency, it is preferable to use bath arrangement CNTs extraction prior to column arrangement, because in the first case sorbent is in contact with the sample for whole experimental time.
5. Two hundred milligrams of carbon nanotubes modified by oxidation (12 hours at room temperature in $8 \text{ mol dm}^{-3} \text{ HNO}_3$) were sufficient to adsorb $200 \text{ }\mu\text{g}$ of copper from synthetic aqueous medium with 100 % efficiency in the case of the column and a bath arrangement extraction.

Acknowledgements

This work was supported by the Science Grant Agency VEGA projects no. 1/0126/14 and 1/0130/14.

REFERENCES

- [1] A. Stafiej, K. Pryzyska, *Microchem. J.*, 89 (2008) 29–33.
- [2] S. Chen, Ch. Liu, M. Yang, D. Lu, L. Zhu, Z. Wang, *J. Hazard. Mater.*, 170 (2009) 247–251.
- [3] V. Camel, *Spectrochim. Acta B*, 58 (2003) 1177–1233.
- [4] C.F. Poole, A. D. Gunatilleka, R. Sethuraman, *J. Chromatogr. A*, 885 (2000) 17–39.
- [5] K. Pryzyska, *Trend. Anal. Chem.*, 29:7 (2010) 718–727.
- [6] C. H. Latorre, J. Á. Méndez, J. B. García, S. G. Martín, R. M. P. Crecente, *Anal. Chim. Acta*, 749 (2012) 16–35.
- [7] P. Liang, E. Zhao, Z. Q. Ding, D. Du, *Spectrochim. Acta B*, 63 (2008) 714–717.
- [8] R. Sitko, B. Zawisza, E. Malicka, *Trend. Anal. Chem.*, 37 (2012) 22–31.
- [9] G. P. Rao, Ch. Lu, F. Su, *Sep. Purif. Technol.*, 58 (2007) 224–231.
- [10] G. D. Tarigh, F. Shemirani, *Talanta*, 115 (2013) 744–750.
- [11] T. Shamspur, A. Mostafavi, *J. Hazard. Mater.*, 168 (2009) 1548–1553.
- [12] P. Liang, Y. Liu, L. Guo, *Spectrochim. Acta B*, 60 (2005) 125–129.
- [13] D. Afzali, R. Jamshidi, S. Ghaseminezhad, Z. Afzali, *Arabian J. Chem.*, 5 (2012) 461–466.
- [14] S. Ghaseminezhad, D. Afzali, M. Taher, *Talanta*, 80 (2009) 168–172.
- [15] A. V. H. Herrera, M. Á. González-Curbelo, J. Hernández-Borges, M. Á. Rodríguez-Delgado, *Anal. Chim. Acta*, 734 (2012) 1–30.
- [16] M. Tuzen, K. O. Saygi, M. Soylak, *J. Hazard. Mater.*, 152 (2008) 632–639.
- [17] A. Duran, M. Tuzen, M. Soylak, *J. Hazard. Mater.*, 169 (2009) 466–471.
- [18] M. Soylak, O. Ercan, *J. Hazard. Mater.*, 168 (2009) 1527–1531.
- [19] D. Afzali, A. Mostafavi, F. Etemadi, A. Ghazizadeh, *Arabian J. Chem.*, 5 (2012) 187–191.
- [20] Z. Zang, Z. Hu, Z. Li, Q. He, X. Chang, *J. Hazard. Mater.*, 172 (2009) 958–963.